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Spin diffusion in melts of entangled polymers

Fischer E., Kimmich R., Fatkullin N.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

Based on theoretical considerations [N. F. Fatkullin, Sov. Phys. JETP 72, 563 (1991)], immaterial spin diffusion mediated by flip-flop transitions of dipolar coupled spins on different macromolecules was predicted to influence the diffusion coefficient measured in nuclear magnetic resonance field-gradient experiments. In order to test this hypothesis, we have carried out supercon fringe field proton magnetic resonance diffusometry experiments with polyethylene oxide melts (Mw=438 000) using field gradients of up to 60 T/m. The polymer chains were dispersed in a matrix of deuterated chains of an equivalent molecular mass. The time-dependent segment diffusion coefficients measured in the diluted and undiluted polymer coincided for diffusion times below about 200 ms. However, increasing the diffusion time up to 1 s leads to a reduction of the diffusion coefficient in the deuterated matrix by a factor of about 2 relative to the undeuterated system. The long-time diffusion coefficient measured with long polymer chains, which are subject to interchain spin couplings, is obviously strongly influenced by spin diffusion mediated by flip-flop transitions of dipolar coupled spin pairs. This holds true in spite of the relatively long flip-flop time, which is estimated to be of the order 0.1 s.